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Limited influence of nutrient additions to the transformation of dissolved and particulate organic matter from a peatland headwater

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Key Points:

- Nutrients were added to water from a high dissolved organic carbon, nutrient-poor headwater
- The additional nutrients were incorporated into the organic matter structure, but did not stimulate additional degradation
- Isotope analysis supported the hypothesis that organic matter turnover was occurring even if there was no net change in concentration

Abstract

Peatlands are typically rich in labile dissolved and particulate organic matter (DOM and POM) but poor in nutrients; as these peatland waters flow through a catchment they mix with more nutrient-rich but organic matter (OM) poor waters. These new sources of nutrients may lead to increased OM degradation, driving further release of CO_2 to the atmosphere. The aim of this study was to discover if the addition of nutrients changed the rates of peat-derived dissolved and particulate organic carbon (DOC and POC) degradation, or if the additional nutrients were incorporated into the OM structure. The DOM and POM extracted from a peatland stream was characterised at the beginning of the experiment, and after 70-hours and 10-days, from water with and without additional nutrients. Results showed adding nutrients to the water had no significant impact on the rate of degradation of DOC or POC over a 10 day period. There were significant differences in the N content and C:N ratios, as well as other composition variables, of the DOM in the treatments with additional nutrients showing that N was incorporated into the DOM structure, but that nutrient addition did not stimulate significant extra DOM or DOC loss. The N content of POM was not impacted, and isotope analysis, supported the conclusion that DOM turnover was occurring even if there was no net change in DOC concentration due to nutrient addition.

1 Introduction

Peatlands cover less than 3% of the world but store approximately 50% of the global soil carbon (Xu et al., 2018) and are important sources of fluvial organic matter (OM; Billett et al., 2004). Several natural processes, such as erosion of bare peat, cause high concentrations of particulate organic matter (POM) and dissolved organic matter (DOM) in waters draining areas of peat soils (Pawson et al., 2008). POM and DOM from peatlands contain high concentrations of organic carbon, as particulate organic carbon (POC) and dissolved organic carbon (DOC). The concentrations of both DOC and POC are rising in surface waters across the Northern Hemisphere (Rantala et al., 2016), making it more important than ever to understand the ultimate fate of the fluvial organic carbon.

Globally, 5.1 Pg C yr^{-1} enter inland waters from land, of which 3.9 Pg C yr^{-1} is returned to the atmosphere (Drake et al., 2018). For every kg of organic carbon entering the UK fluvial network, 2.95 kg CO_{2eq} yr^{-1} are emitted to the atmosphere; the large emission factor is due to the turnover of organic matter releasing not only CO_2, but also CH_4 and N_2O (Finlay et al., 2016). Therefore, the in-stream processing of peatland DOM and POM is a large source of GHG emissions.

The concentration of DOM and POM, and therefore DOC and POC, change due to in-stream processes such as biodegradation and photodegradation (Moody and Worrall, 2016), and in-situ production of DOM from POM (Evans and Thomas, 2016). Therefore it is highly likely that the composition of the DOM and POM also changes in transit. In-stream POM and DOM can be used as an energy source for microbes (biodegradation), degraded by light (photodegradation), and converted to carbon dioxide (CO_2) which then de-gasses to the atmosphere, contributing to the greenhouse gas (GHG) emissions from peatlands (Worrall et al., 2012). Studies have shown that microbes and light preferentially degrade different DOM structures – biodegradation acts on aliphatic compounds, whereas photodegradation breaks down aromatic compounds (Hansen et al 2016).

Labile DOC is processed quickly in peat streams; the "active fraction", comprised of microbial biomass and plant detritus, and is responsible for the majority of the CO_2 released (Weintraub and Schimel 2003). In photo- and bio-degradation experiments, rates of up to 6.04 mg C L^{-1} hr^{-1} were measured in the first hour, that then decline to 0.07 mg C L^{-1} hr^{-1} after 48 hours (Moody et al., 2013; Brailsford et al., 2019). There is also a high turnover of peat-derived POC; between 38 and 87% was removed over 10-days (Moody et al., 2013). Rate law models for the turnover of fluvial organic matter in streams (such as those proposed and tested by Worrall and Moody, 2014) show DOM turning over between a series of organic matter types, producing CO_2 as it does, and the DOM becoming increasing refractory. Pathways of DOM included in the model were both photo- and non-photo-induced loss and production, and the interaction with POM. The increasing refractory nature of the DOM explains that decreased reaction rates over time, and at no point did the DOM drop to negligible concentrations. The model showed DOM was acting as an energy source but not a nutrient source; increased degradation rates were found to be proportional to the presence of O-containing functional groups but was negatively-correlated to N-functional groups (measured by ^{13}C-nuclear magnetic resonance (NMR); Moody and Worrall, 2017). However, the rate of degradation was compared to the initial composition and not confirmed by examining the final composition. It is likely that the final composition of the DOM would be more reduced, as the turnover of DOM produces CO_2.

Ombrotrophic peatlands are relatively low-nutrient environments, and studies have shown that the low nutrient concentrations in waters draining peatlands limit the potential degradation of DOC (Hulatt et al., 2014; Palmer et al., 2016; Brailsford et al., 2019). Marschner and Kalbitz (2003) reviewed the controls on DOM degradability in soils and suggested that increased nutrient concentrations led to higher DOM degradation rates, with the greatest enhancements occurring when the DOM was N or P poor. They also assessed the structure of DOM, and found that DOM with higher aromatic or alkyl content is harder to degrade, therefore these groups accumulate in DOM in soils. The impact of nutrient addition on consumption of DOC in the Amazon River system showed varied results, with nitrate, phosphate and glucose addition resulting in increased bacterial respiration rates in some rivers, but no difference in others, leading the authors to conclude that the system was C-limited (Amon and Benner, 1996). Similarly, Brailsford et al. (2019) found that adding N and P to peatland water in incubation experiments increased the uptake of ^{14}C-labelled glucose compared with treatments without nutrients, with rates varying between treatments with just N, just P and combined N and P. Nutrient addition did not impact overall biodegradability of DOC in incubation studies of water from thawing permafrost, however the study showed an increased loss of 'fast' biodegradable DOC, suggesting that the composition of DOC was important in determining degradation potential (Abbott et al 2014). Some incubation studies add nutrients to avoid limiting microbial activity (e.g. Moran et al., 2000; Mostovaya et al., 2017), but do not directly measure the impact of this on the DOC concentration or DOM composition. The varying results of these studies all show that the impact of nutrient addition on the rate of DOM degradation is not clearly understood, and further study is needed.

The composition of DOM and POM has been investigated in varied environments and ecosystems, by several methods. Elemental (C:N) and isotopic ratios have been used to distinguish

between autochthonous and allochthonous sources of organic matter (Lobbes et al., 2000). ^{13}C and ^{15}N-NMR have been used to identify structures of selected fractions of natural organic matter (NOM; Lankes et al., 2008). These studies show the potential for using multiple methods to show significant differences in the structure, source and behaviour of DOM and POM in natural freshwaters, and so, in this study we used elemental, isotopic, thermogravimetric and NMR analysis, to assess different aspects of the composition of DOM and POM.

As the production of DOM and POM, and therefore DOC and POC, are biological processes, there is seasonal variation in the concentrations and compositions of both (Dinsmore et al 2013). Additionally, the in-stream processes that act on organic matter, and the nutrient concentrations of the water, are also seasonal (e.g. temperature dependent, Dinsmore et al 2013; light dependent, Moody and Worrall 2016). Therefore it follows that the relationship between nutrient concentrations, DOC and POC degradation rates, and DOM and POM composition will vary seasonally.

Taking into account the knowledge gaps outlined, the aim of this study was to quantify the impact of nutrient addition on DOC and POC degradation, and to characterise the impact of nutrient addition on the DOM and POM composition. We also investigated the differences in the elemental and functional group composition between DOM and POM. We hypothesized that adding nutrients would increase the rate and extent of POC and DOC degradation and loss, and the DOM and POM composition would be more reduced (higher proportion of unsaturated compounds), and contain different functional groups, at the end of experiment.

2 Materials and Methods

2.1 Study site

This study collected water from Cottage Hill Sike, (54.689°N, -2.399°E) a small, peat-covered catchment (0.2 km^2, with 100% peat cover), a tributary of Trout Beck, within the Moor House National Nature Reserve in the UK. The site has been extensively studied since 1954, and is an Environmental Change Network site, with over 20 years of water chemistry and environmental data (Rennie et al., 2017). The mean annual temperature at Moor House is 5.9 °C, and the mean annual rainfall is 2010 mm. There is a gauging station on Trout Beck, where the mean annual discharge is 0.57 $m^3\ s^{-1}$ and the mean annual water temperature is 8.9 °C (Rennie et al., 2017). Within the Trout Beck catchment (11.4 km^2, 90% peat cover) the dominant vegetation types are heather, cotton grass and Sphagnum moss. The residence time of Trout Beck is approximately 4.33 hours (Moody et al 2016). Between 1992 and 2013 the mean DOC concentration at Cottage Hill Sike was 18.87 mg L^{-1}; the mean total N was 0.52 mg L^{-1}; the mean conductivity was 42.94 µS cm^{-1}; the mean pH was 4.37 (Moody et al., 2016; Rennie et al., 2017).

2.2 70-hour and 10-day experiments

To study the degradation of DOC and POC in ambient day/night and temperature conditions, approximately 20 L of stream water from Cottage Hill Sike was poured into a fish tank with a quartz glass lid, and kept outside of the laboratory. Quartz glass allows all light wavelengths to pass through it, and the lid was not air-tight so as to prevent anaerobic conditions developing in the fish tank. The water was kept circulating using a solar-powered pond pump. Photosynthetically active radiation (PAR) and air temperature were recorded at 15-minute intervals next to the fish tank (Skye Instruments, PAR Quantum and temperature probe). A Tiny Tag Aquatic 2 logger (Gemini Data Loggers) was submerged in the tank to record the water temperature at 15-minute intervals. Experiments lasted 10 days, incorporating the in-stream residence time of all UK rivers (Worrall et al., 2014). The experiments were carried out to investigate the effect of nutrient addition over the course of a year (to experience varied DOC and POC concentrations, and DOM and POM compositions) and were conducted 13 times from September 2015 to

July 2016. In the final experiment the nutrients added were ^{15}N-labelled as means of tracing where the nutrients were going during the experiments.

Each experiment spanned 10 days with sub-sampling of the water taking place at hour 0, 1, 2, 8, and then at dawn and dusk on day 2, 3 and 4, up to approximately 70 hours, and then once a day on days 5 to 10 for the 10-day experiments. The water sub-samples were small in volume (> 20 mL) relative to the volume of water in the fish tank; and were filtered to 0.45 μm (Whatman, 28 mm diameter, syringe filter), "fixed" using concentrated sulphuric acid, and analyzed using the wet oxidation method described in Bartlett and Ross (1988). Fixing the samples means that the samples would not further degrade prior to analysis. The measurement of DOC concentration was calibrated using standards of oxalic acid of known concentrations, and only calibration curves with an r^2 of 0.95 or above were used. Replicates were included in the calibration analysis (n = 39, 7-8 replicates per concentration) and the r^2 of the relationship between replicates was 0.9967. Correction factors from Giasson et al (2014) were applied to the DOC concentrations, in order to correct for any measurement bias from the Bartlett and Ross method.

At each sub-sampling time a duplicate sample (approx. 20 mL) was filtered to 0.45 μm and analyzed for anion and cation concentrations, absorbance at 400, 465 and 665 nm, conductivity, pH and water temperature. Fluorine, chlorine, nitrogen as nitrite and nitrate, bromine, sulphur and phosphorous concentrations were measured using suppressed conductivity detection on a Dionex-ICS3000, with an IonPac AS18 column and KOH eluent. Concentrations of chloride, nitrite, nitrate and phosphate were calculated from these. The chloride concentration was used to determine that there was no significant loss of water from the tank via evaporation; as chloride is a conservative ion. There was there was no significant change in the chloride concentration in the water, and therefore minimal loss of water by evaporation. Sodium, ammonium, potassium, magnesium and calcium concentrations were measured using suppressed conductivity detection on a Dionex-ICS3000, with an IonPac CS16 column and isocratic MSA eluent. Absorbance measurements (including colorimetric measurements of DOC) were performed using a UV-Vis spectrophotometer, with a 1 cm cuvette and deionized water blanks. The ratio of absorbance at 465 nm to 665 nm is the E4:E6 ratio, and reflects the humic to fulvic nature of the DOC. The specific absorbance at 400 nm ($SUVA_{400}$) was calculated as the absorbance at 400 nm divided by the DOC concentration.

A third water sub-sample (50-100 mL) was taken and analyzed for suspended sediment concentration, and therefore subsequent POM and POC concentrations. This third sub-sample was filtered through pre-weighed, 0.6 μm filters (Whatman, 47 mm diameter, glass fibre); dried to 105 °C and the filter paper re-weighed to give the concentration of suspended sediment. The filter papers were then combusted for 4 hours at 550 °C, and re-weighed. The mass lost in the furnace equates to the mass of POM, and the carbon content of the POM (measured by elemental analysis, described below) was used to calculate the POC concentration. Ideally larger volumes of water would be used to calculate the POC concentration (at least 300 mL), however smaller volumes were used in order to keep the volume of water in the fish tank as high as possible, to ensure enough water was left to extract the mass of DOM needed for further analysis.

2.3 Nutrient addition

The nutrient addition treatments applied during the experiments:

- 70-hour degradation, exactly as above, with no nutrient addition (named "70C")
- 70-hour degradation, as above, but with a NP nutrient solution added at t_0 (named "70N")
- 10-day degradation, as the 70-hour degradation but extended to 10 days, with no nutrient addition (named "240C")
- 10-day degradation, as the 70-hour degradation but extended to 10 days, with a NP nutrient solution added at t_0 (named "240N")

The nutrient solution contained 16.74 g NH_4NO_3 L^{-1} and 0.28 g $Ca_3(PO_4)_2$ L^{-1}, and 10 mL was added to each tank in the 70N and 240N treatment. To ensure the nutrients were not a limiting factor in the complete processing of DOM and POM, the quantities were calculated to be in excess.

Due to limited equipment availability, all four treatments were not all carried out on all 13 experiments. During the July 2016 experiment (the final nutrient addition experiment), all four treatments were carried out, and the nutrient solution was made using ^{15}N labelled $NH_4{}^{15}NO_3$, to determine if the additional nitrate was incorporated into the DOM and POM.

2.4 DOM and POM sample collection

For the initial composition of the DOM and POM prior to any degradation experiment this study used the same method of sample collection as previous studies at the same site (Moody and Worrall 2017). A large volume sample (at least 20 L) was collected from the Cottage Hill Sike on the day of each degradation experiment. This large volume sample was returned to the laboratory on the day of collection and was allowed to settle, but was not filtered. The supernatant was tapped off above the deposited layer and evaporated to dryness at 80 °C, after which the residue collected for analysis. The temperature of 80 °C was chosen as warm enough to facilitate relatively quick evaporation of the supernatant water, but not so hot as to alter the composition of the DOM. The residue of the evaporation was scraped out of the evaporation dish and collected as dried powder and comprised of the dissolved and colloidal (but not particulate) material, and so is henceforth referred to as DOM. The low ash (inorganic) content of the DOM collected was confirmed by thermogravimetric analysis and elemental analysis (described below), and so no further sample preparation was needed before analysis.

The suspended material that sank to the bottom of the 20 L sample was not added to the evaporation dish and excluded from the subsequent DOM analysis. However, this remaining sample was filtered through a 0.7 µm filter (Whatman, 47 mm diameter, glass fibre, pre-combusted at 550 °C for 4 hours) and the residue collected from the filter papers, dried at 105 °C and ground using a pestle and mortar, classed as POM, and analyzed in the same way as the DOM samples.

Fish tanks were used in the experiments, ensuring that at the end of the experiments there was still sufficient sample volume remaining, such that DOM could be collected in analyzable quantities. Therefore, at the end of the 70-hours, or the 10-days, in the fish tank experiments the remaining water was taken into the laboratory, allowed to settle, and then treated the same as the initial water for DOM and POM collection, i.e. settled with the supernatant evaporated to dryness to collect the DOM, and the settled layer filtered and the POM collected. The initial DOM and POM samples (called "t_0") were compared to those that had been exposed to the day/night cycle for 70 hours (70C and 70N) or 10 days (240C and 240N). Due to very low POM content of the water, some experiments had no 70-hour or 10-day POM sample.

2.5 DOM and POM sample analysis

The DOM and POM samples were analyzed for a range of characteristics that measure the nutrient and redox status of the organic matter. The types of analysis were: elemental composition (elemental analysis for carbon, hydrogen, nitrogen and oxygen, relative functional group composition (solid state ^{13}C NMR, DOM samples only); ^{15}N content (isotope mass spectrometry); and thermal stability (thermogravimetric analysis). All samples were analyzed as in Moody and Worrall (2017).

The elemental analysis was carried out for organic carbon, hydrogen, nitrogen and oxygen (CHNO) content of the POM and DOM samples using a Costech elemental combustion system with pneumatic auto-sampler. The samples were analyzed in triplicate for CHN and separately for O. Samples with a relative standard error of more than 5% were reanalyzed. Standards of acetanilide (C_8H_9NO) were used to calibrate the analyzer, and calibrations with a regression r^2 of less than 0.999 were re-calibrated.

Molar proportions of the four measured elements were calculated from ash and mass-corrected data, assuming 1% for unmeasured sulphur. From the molar concentrations the carbon oxidation state (C_{ox} – Masiello et al., 2008), the oxidative ratio (OR – Masiello et al., 2008), the degree of unsaturation (Ω – McMurry 2004) and the elemental ratios of the samples were calculated. Samples of DOM previously collected from the same site had previously been analyzed for P content (Worrall et al. 2016a). Those samples had a very low P content, and so samples from this experiment did not undergo ICP-OES analysis for P content.

A sub-set of samples were analyzed for the ^{15}N content at the National Environment Isotope Facility at CEH Lancaster. A varying amount of each sample (enough to yield 100 µg nitrogen where possible) was weighed using a high precision micro-balance, (Sartorius Ltd) and sealed into a 6 x 4 mm tin capsule (Elemental microanalysis, Okehampton, UK). Samples were then combusted using an automated Carlo Erba NA1500 elemental analyzer coupled to a Dennis Leigh Technologies Isotope Ratio Mass-Spectrometer. In-house working standards of either natural abundance flour or ^{15}N-enriched flour were analyzed after every twelfth sample, resulting in a maximum analytical precision of 0.41‰ for the natural abundance standard, and 1.94‰ for the ^{15}N-enriched samples (current mean value of 216.93‰). These standards are calibrated against the certified reference material IAEA-N1 (NIST number 8547, National Institute of Standards and Technology, Gaithersburg, USA). For duplicates analyzed, standard deviation was a maximum of 2.17‰. Results are expressed in delta notation; i.e. $\delta^{15}N = [(R_{sample} / R_{standard})/R_{standard}] \times 1000$ (‰) where R is the ratio of ^{15}N to ^{14}N in the sample and standard accordingly. All $\delta^{15}N$ results are expressed relative to the international standard of atmospheric air. In total, the ^{15}N content of 31 organic matter samples were analyzed:

- Five DOM and five POM samples collected from the ^{15}N addition experiment (t_0, 70C and 70N, 240C and 240N)
- Two DOM and five POM samples from nutrient addition experiments (without ^{15}N addition). Samples were chosen that had similar N content to the samples from the same treatments. DOM samples from November 2015 (70N, 240N treatments) and POM samples from May 2016 (t_0), September 2015 (t_0), and November 2015 (t_0, 70N, 240N).
- An additional 14 DOM t_0 samples from a previous experiment were included in the analysis. These were collected by the same method as above, approximately monthly from CHS between October 2011 and January 2013. These provided a background concentration of ^{15}N in the DOM samples.

The ^{13}C solid-state NMR was used to identify the main functional groups of the DOM samples. Solid-state ^{13}C-NMR spectra were recorded at 100.56 MHz using a Varian VNMRS spectrometer and a 4 mm magic-angle spinning probe at the EPSRC UK National Solid-state NMR Service at Durham University, using the same method as Moody et al. (2018). The maximum peak height in each eight chemical shift ranges (0-45 ppm C-alkyl; 45-65 ppm N-alkyl and methoxyl-C; 65-95 ppm O-alkyl-C; 95-110 ppm O_2-alkyl-C; 110-145 aromatic/unsaturated C; 145-160 ppm phenolic C; 160-190 ppm carboxyl/amide C; 190-220 ppm aldehyde/ketone C; Baldock and Skjemstad 2000; Hockaday et al 2009) was divided by the percentage carbon content (from the elemental analysis) to get a relative peak height for each functional group type of carbon observed. The proportion of the total carbon that was attributed to each functional group was calculated. The functional groups can be considered as oxic (e.g. O_2-alkyl), reduced (aromatic/unsaturated C) and nutrient containing (N-alkyl).

The thermogravimetric analysis (TGA) was carried out using an STA i TGH 1200, with a N_2 atmosphere. The balance in the TGA recorded the exact starting weight; weight loss was reported as a percentage of the starting weight. The starting temperature was 25 °C, and was ramped up 20 °C a minute to 1000°C. The weight at 550 °C ("loss on ignition") and weight at 1000 °C ("final weight") were included in the analysis, reported as percentage of the starting weight that remained (e.g. smaller numbers indicate more organic matter was lost). Oxidized C within DOM would be expected to be lost at lower

temperatures than reduced C and so cumulative loss over a TGA spectra represents change in the redox status of the C in DOM. The measured TGA spectra was analyzed as per the approach and method reported in Worrall et al. (2017) but none of the derived characteristics or relationships proved significant and so these results will not be discussed further. The links between initial composition of DOM and POM and the rates of DOC and POC degradation were not discussed here (see Moody and Worrall 2017).

2.6 Statistical methodology

The seasonal variation on the initial and final DOC and POC concentrations was investigated – relating the total concentration changes to the temperature and PAR experienced during each experiment. Each months' degradation experiment was considered independent of the previous and next experiment, as the residence time of the stream is less than the time between sampling (based on the residence time of Trout Beck (4.33 hours)). Within each months' degradation experiment, the sampling times were not independent of each other, and so repeated measures analyses were used. The change in the DOC concentrations were analyzed using a repeated measures ANOVA, with treatment (which had four levels 70C, 70N, 240C, 240N) and experiment number (approximately one per month for 13 months) as factors, and sample time as the repeated factor. Sample time was expressed as the average number of hours since start of experiment (with 16 levels – henceforward referred to as t_0, t_1, t_2, t_5, t_{19}, t_{28}, t_{43}, t_{52}, t_{67}, t_{76}, t_{102}, t_{142}, t_{166}, t_{189}, t_{214} and t_{236} – with t_x where x is the number of hours since the start of the experiment). The 16 samples were taken on the first day, and dawn and dusk on day 2, 3 and 4, and on days 5-10. As the time of dawn and dusk varies across the year and the 13 experiments were deliberately carried out to include seasonal variation, timings are given as averages of the number of hours after the experiment started. This analysis was performed on the relative DOC concentration data, where the concentration was calculated as a ratio of the initial (t_0) DOC concentration in that particular experiment.

Paired t-tests were used to investigate differences in the POC and nutrient concentrations between the beginning (t_0) and end of the experiment (t_{67} for 70C and 70N treatments, t_{236} for 240C and 240N treatments). Paired t-tests were carried out to look for differences between 'before' (t_0) and 'after' (t_{67} and t_{236}) composition variables of the DOM and POM. This analysis was done for each type of material (DOM or POM) and each treatment (70C, 70N, 240C, 240N) separately.

For each of the ANOVA described above all the data were tested for homogeneity of variance and normality using the Levene and Anderson & Darling tests respectively. If the data failed either of these tests then the data were log-transformed and re-tested – further transformations did not prove necessary. All statistical results are reported as statistically different if probability of no difference was less than 5% ($p < 0.05$).

3 Results

3.1 Environmental Conditions

The highest PAR the water samples were exposed to during a 15-minute interval was 1131 µmol m^{-2} s^{-1}. The cumulative PAR (the sum of every 15 minute PAR during the 240 hours) ranged from 1796 to 37700 µmol m^{-2} (Figure 1). The temperature ranged between -1.72 and 21.73 °C, and the average range was 11.25 °C (standard deviation 1.36). There was seasonal variation in the dataset – the highest PAR and air temperatures were in July, and the lowest were in December and February.

The initial concentrations of DOC varied between 37.82 and 72.68 mg C L^{-1} (average 57.28 ± 11.07 mg C L^{-1}), and the initial POC concentration varied between 0.47 and 19.43 mg C L^{-1} (average 3.51 ± 5.37 mg C L^{-1}). There was no clear seasonal cycle in the initial concentrations, but the DOC concentration was lower and the POC concentration was higher in winter than the rest of the year (Figure 1, experiment numbers 6-9).

Comparing the final POC concentrations in each experiment by treatment showed no clear relationships with minimum or maximum temperature, or cumulative PAR experienced during the experiment. There were also no relationships between these environmental variables and the final DOC concentration in the 240C, 240N and 70N treatments. There was positive, but not significant, relationship between the final DOC concentration in the 70C treatment and the cumulative PAR ($p = 0.07$, $r^2 = 0.51$, $n = 7$). The final DOC concentration in the 70C treatment had a significant positive relationship with both the minimum ($p = 0.003$, $r^2 = 0.86$, $n = 7$) and the maximum temperature ($p = 0.02$, $r^2 = 0.70$, $n = 7$) experienced during the experiment. These relationships were not present in the 240C treatment DOC concentrations, suggesting that temperature (and possibly cumulative PAR) do initially impact the DOC concentration changes over 70-hours but were not a significant influence on the DOC over 10-days.

Further analysis of the impact on environmental conditions on the DOC and POC concentrations during the experiments (rather than the final DOC and POC concentrations) showed there were significant ($p < 0.05$), weakly positive relationships between the DOC concentrations and the air and water temperature, and PAR. The environmental conditions explained up to 13.6 % of the variation in the DOC concentration. These show that at each sampling time point, if the temperature (air or water) or PAR were high, then the DOC concentration was also high. There was no corresponding significant relationship between the POC concentrations and the air/water temperature or PAR conditions.

3.2 POC and DOC concentration changes

Across all experiments, on average 58% of the DOC and 82% of the POC was lost over the 70 hour experiments; and on average 49% of the DOC and 66% of the POC was lost over the 240 hour experiments (Table 1; Figure 2a, 2b, S1 and S2). The DOC concentrations decreased steadily during the first 50 hours, then stabilized around 30 mg C L^{-1} for the remainder of the experiment. Both the DOC and POC concentrations increased at times during the experiments. Most notably, the average t_{236} POC concentration is much higher than the concentrations for the previous samples (Figure 2b and S2). As the water was unfiltered, the production of DOC and POC was possible, as processes such as flocculation, photosynthesis and degradation can change the OC concentrations. However there was a net loss of both DOC and POC over the total time of the experiment.

The repeated measures ANOVA on the relative DOC concentration was carried out, comparing treatments with nutrients (70N and 240N) and treatments without (70C and 240C), up to and including t_{67}. There were no significant differences between treatments or experiment number. There were significant differences between sample times ($p < 0.01$). The results of analysis of each sampling time step showed there were significant differences between the experiment numbers at sampling times t_1, t_2 and t_4 (all were significantly higher than subsequent times). The interaction between treatment and sample time was not significant for the DOC concentrations, and there was no systematic pattern to this interaction (Figures 2a, S1).

The repeated measures ANOVA on the relative DOC concentration was carried out on 240C and 240N treatments up to and including t_{236}. There were no significant differences between treatments or experiment number, or the repeated measure of sample time. The lack of significant treatment effect shows that there was no significant effect of nutrient addition on the DOC concentrations.

The paired t-test showed there were no significant differences between the beginning (t_0) and end (t_{236}) POC concentration in the 240C or 240N treatments. Likewise, there were no significant differences between the beginning (t_0) and end (t_{67}) POC concentration in the 70C or 70N treatments.

The absorbance at 400 nm and E4:E6 ratio were relatively constant throughout the 70-hours and 10-days of each experiment, showing that the water colour and fractions of humic to fulvic acid were not impacted by the nutrient addition. The specific absorbance at 400 nm ($SUVA_{400}$) increased steadily (Figure 2c). The increase in $SUVA_{400}$ was slightly higher in the 70N treatment than the 70C, and in the

240N treatment than the 240C. $SUVA_{400}$ was significantly higher ($p < 0.01$) at the end (t_{67} or t_{236}) than the beginning (t_0) of the experiment in all four treatments. The DOC concentration decreased but the colour (absorbance at 400 nm) did not, indicating that the DOC became more colored as it decreased.

3.3 Nutrient concentrations

Before nutrient addition, the average ammonium, nitrate, calcium and phosphate concentrations were 0.11, 3.971.56 and 1.75 mg L^{-1}, respectively. At t_1, after nutrient addition, the average ammonium, nitrate, calcium and phosphate concentrations in the 70N and 240N treatments were 1.71, 27.37, 1.10 and 2.68 mg L^{-1}. At t_1 in the treatments without nutrient addition (70C and 240C) the average concentrations were 0.20, 2.17, 1.36 and 0.55 mg L^{-1}. The concentrations the N-species at t_1 was lower than the amounts added, suggesting rapid turnover. As the 'excess' N (difference between the amount added and the amount measured at t_1) was not present in any form of measured N, it is likely this 'excess' N was denitrified and lost to the atmosphere as N_2, or very rapidly incorporated into the DOM and/or POM structures.

The nitrate concentrations were higher in the 240N and 70N treatments than in the 240C and 70C treatments (Figure 3a), and on average were at least five times higher. The paired t-test showed that there no significant differences in the nitrate concentration between the start and end of the experiments (t_0 and t_{67} or t_{236} samples) in the 70C and 240C treatments. There were significantly higher concentrations of nitrate in the 70N and 240N treatments at t_{67} and t_{236} than at t_0 ($p < 0.01$; before nutrient addition), but not between t_{67} and t_{236} and t_1 (after nutrient was added). This showed that the nutrient addition significantly increased the nitrate concentration, but there was no significant difference between the concentration immediately after addition (at t_1) and at the end of the experiment. There were, however, decreases and increases during the course of the experiment, suggesting that the nitrate was more available in the water (and therefore analyzed as dissolved nitrate) at various points during the experiments.

The ammonium concentrations were higher in the 240N and 70N treatments than in the 240C and 70C treatments, and on average were nine times higher (Figure 3b). The phosphorous concentrations were generally so low they were below the detection limit of the analyzer (0.02 mg L^{-1}), resulting in only 20 measurements, none of which were in the 240C treatment (Figure 3c). The average phosphate values for the 240N (2.21 mg L^{-1}) and 70N (2.41 mg L^{-1}) treatments were higher than the values for the 70C treatment (1.24 mg L^{-1}); however there were not enough data for t-tests on the ammonium or phosphorous The nitrite concentrations in the water from all treatments was also analyzed, however the concentrations was always below the detection limit of the analyzer (0.01 mg L^{-1}), so no data were recorded. As the majority of the total N species measured was nitrate (between 75 and 100 %), the trend of the total N content was the same as the nitrate results, above.

3.4 DOM composition changes

The mean elemental composition, stoichiometry and C:N ratio showed that the composition of the DOM varied with both time and nutrient addition (Table 2; Figure 4a-c). The t-test results show that the addition of nutrients changed the composition of the DOM in both the 70-hour and 10-day experiments with nutrient addition. For the 70C treatment, between t_0 and t_{67}, there were no significant differences for any composition variables. For the 70N treatment, between t_0 and t_{67}, there were significant increases in N (average increase from 0.11 to 0.22 moles; $p < 0.0001$; Figure 4a), and significant decreases in C:N (average decrease from 21 to 10; $p = 0.0110$) and proportion of aromatic-C (average decrease from 10.6 to 10 %; $p = 0.0192$; Figure 4c). For the 240C treatment, between t_0 and t_{236}, there were no significant differences for any composition variables. For the 240N treatment, between t_0 and t_{236}, there were significant increases in the N (average increase from 0.11 to 0.20 moles; $p = 0.0030$; Figure 4a) and C_{ox} (average increase from 0.48 to 1.78; $p = 0.0041$; Figure 4b), and significant decreases in the C (average decrease from 2.61 to 1.89 moles; $p = 0.0094$; Figure 4a), C:N (average decrease from 25 to 11; p =

0.0002), OR (average decrease from 0.91 to 0.666; p = 0.0101; Figure 4b) and the degree of unsaturation (Ω; average decrease from 2.07 to 1.59; p = 0.0144; Figure 4b). There were no significant t-test results for H, O, final weight or loss on ignition data, or for the seven other C functional groups (C-alkyl, N-alkyl, O-alkyl, O_2-alkyl, phenolic-C, aldehyde-C or carboxyl-C), showing no significant changes in these variables between the t_0 and any final DOM sample composition.

3.5 POM composition changes

The mean elemental composition, stoichiometry and C:N ratio of the POM composition show it varied with both time and nutrient addition (Table 3, Figure 5a, 5b). For the 70C treatment, between t_0 and t_{67}, there were no significant changes in POM composition. For the 70N treatment, between t_0 and t_{67}, there was a significant decrease in H (average decrease from 4.67 to 3.97 moles; p = 0.0002; Figure 5a) but there were no other significant changes in composition. The degree of unsaturation increased; it is likely that there was a change in structure from C-C single bonds to double bonds, as the hydrogen content decreased significantly. For the 240C treatment, between t_0 and t_{236}, there were no significant differences for any composition variables. For the 240N treatment, between t_0 and t_{236}, there were significant decreases in C (average decrease from 2.61 to 1.89 moles; p = 0.0222; Figure 5a), and H (average decrease from 2.96 to 2.40 moles; p = 0.0252; Figure 5a), but no significant change in the N or O content. The change in C_{ox}, OR and degree of unsaturation (but no significant differences) suggested that there was change in the structure of the organic matter, (reflected in the significant decrease in the LOI%; $p < 0.01$), but not enough to be significant. The LOI% weight was significantly different (average increase from 50 to 64 %; p = 0.0013)

3.6 Isotope analysis

The results of the isotope analysis are shown in Table 4, and Figures 4d, 5c, S3 and S4. The average N content and $\delta^{15}N‰$ are higher in samples with added nutrient solution, and higher still in the July 2016 samples with the added $NH_4{}^{15}NO_3$. Due to the small sample numbers, an ANOVA was carried out that only compared the DOM samples before nutrient addition (t_0) to the grouped 70N and 240N samples (both ^{15}N labelled and not; n = 4), and found a significantly higher $\delta^{15}N‰$ in the 70N/240N group of samples (p = 0.019). The same analysis on the POM samples found no significant difference in the $\delta^{15}N‰$ content of the POM (p = 0.1447). These results are in line with the N content of the DOM and POM samples – there were significant increases in the N content of the DOM samples in the 70N and 240N treatments, but not in the POM samples. However, the results of the nutrient concentrations show that the total N and nitrate concentrations do not change significantly between t_1 and the end of the experiments (t_{67} and t_{236}), therefore the increase in N content either took place incredibly rapidly between nutrient addition (after t_0) and the t_1 sample collection, or the N content increase in DOM was not directly a simple response to the nutrient addition.

4 Discussion

This study has hypothesized that turnover of DOM and POM in the nutrient-poor streams of peat-covered headwater is limited by the lack of nutrients and so as these DOM-rich waters encounter greater supplies of nutrients as they transit through a catchment, DOM degradation will increase. However, this study found no significant change in DOM or POM degradation rate or extent when nutrients were added. The changes in DOM and POM composition don't clearly show that the material is mostly oxidized or reduced over time; there are changes in composition that indicate it is most likely a combination of both. The nutrient concentrations were significantly increased by the addition of nutrients, but then did not change throughout the experiments, suggesting that the nutrient concentrations were not necessarily limiting the DOC and POC degradation. The incorporation of additional N into the DOM (N content

doubled, from 0.11 to 0.22 moles over 70 hours, and from 0.11 to 0.20 over 10 days) structure shows the nutrients did have some impact, but not to the extent hypothesized.

4.1 DOM composition

The composition of the DOM was significantly altered by the addition of nutrients, causing an increase in N content of DOM over both 70-hours and 10-days, but there were no significant changes in the treatments without nutrient addition. These results are similar to those of Brailsford et al. (2019) who found that adding nutrients to upland water had no significant effect on the cumulative CO_2 emissions compared with treatments without nutrients after 168 hours. Similarly to this study, there were differences at earlier sampling points, but at the end of the experiment there were no significant effects of the N and P addition. Nutrient enrichment was shown to impact on both DOC concentration and DOM composition in peat headwater streams by Fovet et al (2020). They showed both consumption and production of DOM, in degradation experiments with and without nutrient addition. Nutrient addition increased DOM production in low nutrient peat stream water, but the effect of multiple competing autotrophic and heterotrophic processes was strongly influenced by the DOM composition and environmental factors, showing the importance of both bio and photo degradation on organic matter (Fovet et al 2020).

Studies have found an impact of the C:N ratios, or nutrient status, on the carbon cycling in a catchment or ecosystem. Armstrong et al (2015) showed that peat C:N ratios and plant functional types influenced the rates of C gas emissions from peat surfaces, specifically P_{cal} (photosynthesis, calculated by subtracting ecosystem respiration from net ecosystem exchange) and methane emissions, and affected the relationship these processes had with air temperature. In a study of water residence times, Köhler et al (2013) showed that the DOC:DON decreases with increasing residence time, as DOM is transformed from N-poor to N-rich through metabolism in the river network – this would be in line with what was observed in this study. Vonk et al (2015) found that high N content in water correlated with high concentrations of biodegradable DOC, but their study would suggest excess autochthonous production of DOM is stimulated by presence of nutrient which would change the composition of the bulk DOM but would also maintain the DOM concentration. Similarly, Evans et al. (2017) in a study of DOC in lakes showed that eutrophic lakes were more likely to be net sources of DOC, while the oligotrophic waterbodies were net sinks of DOC.

The C:N ratios found in this study (between 9 and 23) are similar to those found in other studies of peat-derived DOM and POM, but much lower than those of peat, or of the vegetation found on the peat (25 to 29 (DOM and POM), median of 52 (peat), and 37 to 58 (vegetation); Armstrong et al., 2015; Clay and Worrall, 2015; Moody et al., 2018). The values are generally higher than those of mineral soils (12.6; Clay and Worrall, 2015), or POM from various UK rivers (9.2 to 14.3; Worrall et al., 2016b). The results show that, despite the small changes in nitrate and total N concentrations in the water, N was incorporated into the DOM from the additional nutrients supplied, however the resulting C:N ratios are still not as low as those found in mineral soils; possibly the concentrations of nutrients added was simply not high enough to impact the degradation of DOC.

4.2 POM composition

Nutrient addition resulted in significant alterations to the POM composition over both 70-hours and 10-days, but not to the N content. The changes were limited to the C and H content, and the percentage mass lost on ignition (a proxy for the total organic content of the matter). There were no significant changes in POM composition in the treatments without nutrient addition, suggesting that the changes that did occur were due to nutrient addition, but not directly impacting the N content of POM. The lack of significant impact of nutrient addition upon DOC or POC concentration while a significant change in the composition of the DOM and POM suggest that over time a dynamic pseudo-equilibrium is occurring. We observed no nutrient-driven change in DOC or POC concentration after 70 hours or 10 days (but

498 significant decrease in both DOC and POC over time), but could show that the DOM and POM
499 composition did change over time. The ^{15}N isotope analysis showed that N was being incorporated in to
500 the DOM and POM compounds, with no corresponding change in concentration. The organic matter
501 turnover is resulting in compounds of different molecular structures and composition, without changing
502 the overall concentration of organic carbon. We hypothesize that the DOM and POM are becoming
503 dominated by more microbial, autochthonous compounds, shifting from allochthonous DOM and POM. It
504 is likely that the organic matter in the water was undergoing both photo and biodegradation. The DOM
505 composition showed a proportional increase in C-alkyl-C in the 240C treatment, and decrease in
506 aromatic-C in the 70N treatment, and phenolic-C in the 240C treatment, suggested that photodegradation
507 was the dominant process, resulting in increased availability of smaller molecular weight compounds for
508 microbial growth (Hansen et al., 2016).

509 4.3 Limitations

510 Using multiple methods of analysis on the water and OM samples provided some conflicting results. The
511 $SUVA_{400}$ of the water increased throughout the experiment in all four treatments, indicating the water
512 became more colored. The compounds thought to be responsible for the majority of colored DOM are the
513 aromatic and phenolic compounds. The results showed that the aromatic and phenolic proportion of the
514 DOM collected from the water decreased in three of the four treatments (but increased in the fourth).
515 Previous studies have used $SUVA_{400}$ (and $SUVA_{254}$) as a proxy measure for CDOM (colored DOM) and
516 aromaticity (e.g. Koehler et al. 2016; Allesson et al. 2020). In this study, within each treatment, there
517 were no significant relationships between aromatic or phenolic proportions and $SUVA_{400}$; although most
518 relationships were weakly negative (n = 4-8, dependent on treatment). It is possible the DOM analyzed in
519 this study contained uncolored aromatic and phenolic compounds, or that there are competing processes
520 for the colored/uncolored fractions of DOM, or that $SUVA_{400}$ isn't as good a proxy for aromaticity as
521 $SUVA_{254}$ (Weishaar et al. 2003). The increase in $SUVA_{400}$, and therefore the water color, over the course
522 of the experiments also implies a change in the degradation processes, as colored DOM is less susceptible
523 to photodegradation (Fovet et al 2020). The colorimetric method for determining DOC
524 concentration (the 'Bartlett and Ross' method) has been compared to carbon analyzer methods by
525 Giasson et al., (2014), who presented correction factors to apply to colorimetric measurements. These
526 account for the high variability in carbon compounds found in natural waters that may not be measured as
527 accurately by the colorimetric method, compared to carbon analyzers. The correction factors for peat soil
528 water suggested by Giasson et al., (2014) had the highest r^2 of all soil types tested (0.87), and these were
529 applied to the DOC concentrations measured by this study. The small volumes of water used for POC
530 analysis between the beginning and end of the experiment mean that the concentrations reported were
531 susceptible to slight changes in the accuracy of the balance used to weigh the filter papers at every step.
532 However, precautions were taken to ensure the balance was as accurate as possible – the balance on a
533 sand table, levelled every use, and reset to zero and wiped clean between each sample. These measures
534 have ensured the data reported are as accurate and reliable as possible. Statistical analysis was only
535 carried out on the beginning and end water samples, where a larger volume of water was used to
536 determine the POC concentration.

537 The study had hypothesized that as DOM degrades in transit through the river network that it
538 would become more reduced and although this was true for the POM analyzed in this experiment it was
539 not true for the DOM. Given the significant N addition observed in this study it is possible that the
540 increase in C_{ox} is due to the addition of N into the composition of the DOM. However, examining the
541 average stoichiometric composition of the DOM at the end of each treatment shows that in the 70N and
542 240N experiment the DOC could only have become more oxidized (increased C_{ox}) because of O addition
543 and not just N addition.

5 Conclusions

The study showed that there was no significant effect on the extent or rate of DOC or POC turnover in streams draining peatlands when nutrients were added. Although there was no significant changes in organic carbon concentrations, there were significant changes in the DOM and POM composition with nutrient addition. With the addition of nutrients the DOM composition showed significant increases in N content, and significant decreases in the C:N, and the POM composition showed significant decreases in H content, over timescales up to 10-days.

These findings show that the waters transiting from low nutrient headwaters will not experience enhanced organic carbon turnover as they mix with higher nutrients waters downstream. The results show that organic matter reaches a dynamic equilibrium in which overall concentration of organic carbon does not change but composition of the organic matter evolves.

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Figure Captions

Figure 1. The initial DOC and POC concentrations (mg C L^{-1}), the minimum and maximum air temperature (°C) and cumulative PAR (µmol m^{-2}) for each experiment.

Figure 2. The (a) average relative DOC concentrations, relative to the t_0 concentration; (b) the average POC concentrations, and (c) the average $SUVA_{400}$, of all treatments, across the 240 hours of the experiment. Error bars are the standard errors. The average values include all four treatments and all experiments, as there were no significant differences between treatments or experiment numbers.

Figure 3. The average (a) nitrate, (b) ammonium and (c) phosphate concentrations in the water over the 240 hours of the experiment for all four treatments. Error bars are the standard errors.

Figure 4. (a) The average N, C, H and O composition, (b) the C_{ox}, OR and degree of unsaturation, and (c) the proportion of C in each functional C group in the DOM samples. Error bars are the standard errors. (d) The $\delta^{15}N‰$ of the DOM samples, with and without ^{15}N addition. For the '15N not added' data, there were 14 t_0 DOM samples (mean value shown), and one sample for each t_{67} and t_{236} data point. For the '15N added' data, there is one sample per treatment and time.

Figure 5. (a) The average N, C, H and O composition, and (b) the C_{ox}, OR and degree of unsaturation, of the POM samples. Error bars are the standard errors. (c) The $\delta^{15}N‰$ of the POM samples, with and without ^{15}N addition. For the '15N not added' data, there were three t_0 POM samples (mean value shown), and one sample for each t_{67} and t_{236} data point. For the '15N added' data, there is one sample per treatment and time.